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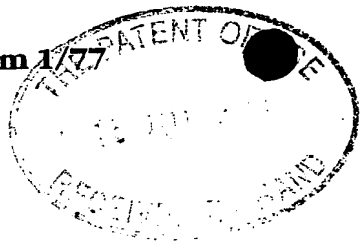

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Request for grant of a patent

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15 JUL 1998

The Patent Office
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1. Your reference — WBH

2. Patent application number *(The Patent Office will fill in this part)* — **9815357.0**

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

TSL Group PLC
P.O.BOX 6,
WALLSEND,
TYNE AND WEAR
NE28 6DG

Patents ADP number *(if you know it)*

If the applicant is a corporate body, give the country/state of its incorporation — UNITED KINGDOM 4028130001

4. Title of the invention

IMPROVEMENTS IN AND RELATING TO THE MANUFACTURE OF SYNTHETIC VITREOUS SILICA INGOT

5. Name of your agent *(if you have one)*

J.Y. & G.W. JOHNSON

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

KINGSBOURNE HOUSE,
229-231 HIGH HOLBORN,
LONDON WC1V 7DP

Patents ADP number *(if you know it)* — 976001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*

a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
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Continuation sheets of this form	
Description	11
Claim(s)	8
Abstract	
Drawing(s)	4 +4

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Request for preliminary examination and search *(Patents Form 9/77)*	
Request for substantive examination *(Patents Form 10/77)*	
Any other documents *(please specify)*	

11. I/We request the grant of a patent on the basis of this application.

Signature J Y k G W Johnson Date 15.7.98.

12. Name and daytime telephone number of person to contact in the United Kingdom

Mr. William Hanson
0171 405 0356

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IMPROVEMENTS IN AND RELATING TO THE MANUFACTURE OF SYNTHETIC VITREOUS SILICA INGOT

Fused quartz glasses, typically made by fusion of refined natural quartz crystal powders, are widely used in the optical, optical fibre and semiconductor industries for their optical properties, chemical resistance, thermal stability or other properties.

In some critical applications, the impurities or inhomogeneities resulting from the use of a natural crystal feedstock may be unacceptable, and then it becomes necessary to substitute a synthetically produced material. Sometimes this may be a synthetically produced powder, but more generally the highest grade vitreous silica products are made by vapour deposition. Thus a vapourised precursor compound of silicon is fed to a synthesis flame where it is oxidised or hydrolised to form a stream of silica fume or a flow of micro-particles of silica which is caused to deposit either as a porous silica soot body, which may be dehydrated or doped by heating in a suitable atmosphere, and then sintered to pore-free glass, or alternatively by deposition at such a temperature that the silica deposit sinters directly to a transparent glass.

The latter process, often called the direct deposition process, yields glass of relatively high OH (hydroxyl content), typically 800-1200ppM by weight, but this is acceptable for many applications, for optical components such as prisms, lenses etc., for larger articles such as windows of furnaces or spacecraft etc., for mirrors, and for the manufacture of photomasks, i.e., the plates which carry the images to be imprinted by a photolithographic process on a silicon wafer, during the manufacture of microcircuits.

The direct deposition process may be operated in either of two modes. In the first of these, shown in Figure 1 of the accompanying drawings, a burner 11 provides a synthesis flame 12, typically an oxy-hydrogen flame, and is fed, via a central duct 11a with a stream of precursor material. The precursor material can be one or more gaseous chlorosilanes, (e.g. silicon tetrachloride), but more recently chlorine-free precursors have been finding favour. The silicon compound is oxidised or hydrolysed to form a stream of silica fume or a flow of micro-particles of silica which is directed on a substrate forming the domed end 13a of a rotating cylindrical ingot 13, supported within a furnace structure 14. A substantial proportion of the silica generated in the flame deposits on the substrate which is slowly withdrawn (in direction Z) from the furnace, preferably maintaining a substantially constant burner-to-substrate distance. The silica is deposited on the substrate at such a temperature that it sinters directly to transparent, pore-free glass. The ingot may be rotating about a horizontal, vertical or other axis, and may be subjected to oscillatory movement on either or both axes (X and/or Y) perpendicular to that of rotation to spread the thermal load on the ingot end 13a, and thus to increase the homogeneity of the glass deposited or to control the cross-sectional shape of the ingot.

A second geometrical arrangement used for collecting glass by direct deposition is shown in Figure 2 of the accompanying drawings. This employs a rotating shallow refractory crucible 21, typically lined with zircon or zirconia-based refractory bricks, mounted on a turntable 22. The bottom of the shallow crucible is typically lined initially with a layer of high purity quartz or quartz glass powder 23, or alternatively crushed synthetic vitreous silica glass for maximum purity. Over this crucible is mounted a refractory roof 24 which carries one or more synthesis burners 25. The crucible may be between 1 and 2 metres in diameter and under these circumstances a significant number of burners may be employed. These serve both to heat the crucible to a

temperature above the melting point of silica, and also as generators of synthesis flames 26, each of which deposits a stream of silica fume or soot on the surface of a molten glass pool 27 which is generated in the crucible. After an appropriate thickness of glass has been so generated, the crucible is allowed to cool, the refractory walls are removed, and the disk-shaped ingot of glass is taken away to be cut, machined or otherwise formed into the required shape.

The process of Figure 1 can be used to generate a cylindrical (e.g. circular cylindrical) ingot. This may be of a size suitable for conversion into cylindrical sections if required, e.g., for lenses or mirror blanks, or may be converted by further thermal processes to rod or tube products. However for some applications a cylindrical shape may be an unsuitable starting material. Thus for certain applications where a series of square or rectangular products is required, for example for photomask substrates, these are either machined from an oversize ingot, with evident wastage, or alternatively the cylindrical ingot is re-shaped, for example by heating to softening temperature within a graphite mould of appropriate internal dimensions and, by slumping under its own weight, or by application of pressure, to force the softened silica to take up the shape of the mould. After cooling, the re-shaped ingot may be cut into slices of the desired dimensions. This secondary operation is costly and results in material losses.

Where such shapes are to be cut from one of the large disk-shaped ingots generated by the crucible process of Figure 2, this involves extensive cutting operations, and again much wastage. It may also be necessary to reject material of unsatisfactory quality, due, for example, to contamination from the refractories of the furnace roof, or from the crucible itself.

Thus for certain shapes of product, notably those of square cross-section, neither of the two major manufacturing

methods yields an ingot which may be used directly, and with high materials efficiency. Furthermore neither permit continuous operation as would be desirable for more economical operation, since both are essentially batch processes.

There is thus a requirement for a direct deposition process for synthetic vitreous silica glass, which can be operated continuously and which will generate an ingot of predetermined cross-sectional dimensions, i.e., round, square, rectangular, or other.

This invention seeks to meet that requirement by providing an improved method of forming a shaped body of synthetic vitreous silica glass and an improved furnace for the manufacture of such a shaped body.

According to one aspect of the invention a method of forming a shaped body of synthetic vitreous silica glass includes the steps of generating a stream of synthetic silica particles in at least one synthesis burner, directing the synthetic silica particles onto a mass of molten silica contained in a refractory enclosure, part of the boundary of which defines a shaping orifice, and removing the generated synthetic silica from the enclosure through the orifice as a shaped ingot.

Conveniently the shaping orifice is located at the lowest part of the mass in the enclosure and the removal involves positively withdrawing the ingot from below, preferably, at a rate substantially similar to that at which synthetic silica is being added to the mass.

Preferably, the burner(s) serve(s) both to generate the synthetic silica in particulate form and to heat the melt so that the silica sinters directly to glass in the mass. Optionally additional heat may be imparted by further heating means.

According to a further aspect of the invention a furnace for the continuous manufacture of a synthetic vitreous silica ingot by direct deposition from the vapour phase, comprises a furnace enclosure, one or more synthesis burners extending into the enclosure, means to feed oxygen, fuel and silicon-containing precursor material to each burner to generate a flame which is directed onto the surface of a melt of synthetic vitreous silica contained in the furnace enclosure, the flame or flames serving both to heat the melt and to generate a stream of silica which adds to the melt the furnace enclosure including a die which incorporates an orifice through which the glass ingot is extruded by an arrangement of moveable clamps contacting the ingot downstream of the orifice.

Optionally, the furnace enclosure with its die, the ingot and the arrangement of clamps may be rotated synchronously to provide a deposited glass of improved homogeneity.

Again optionally, the arrangement of clamps may be moved to and fro horizontally in an x-direction, or alternatively in orthogonally disposed x- and y- directions, to permit spreading of the pattern of deposited glass from the one or more burners.

Alternatively a spreading of the pattern of deposited silica can be achieved by like movement of a burner array, and/or the furnace enclosure.

The following invention will now be more fully described, by way of example, with reference to Figures 3 and 4 of the accompanying drawings.

In one embodiment of the invention, as illustrated in Figure 3, the apparatus comprises a furnace enclosure 31 lined with refractory brick and supporting a roof 32 also made of suitable refractory material. One or more burners 33, project

through this roof. These burners may be made from metal or quartz glass, and are fed with a fuel gas (e.g., hydrogen and/or natural gas etc), with oxygen, and with the vapour of an appropriate compound of silicon, which on oxidation and/or hydrolysis yields a stream of micro-particles of silica fume, which stream is directed at the surface of a mass 34 of glass melt contained in a refractory enclosure or container, 35.

The precursor material can be silicon tetrachloride or other halosilane, in which case the product gases contain the noxious and corrosive by-products, hydrochloric acid and chlorine. These must be handled with care, and scrubbed with appropriate gas-cleaning equipment before release to atmosphere. Alternatively, if the precursor material is a chlorine-free silicon compound such as a siloxane or alkoxysilane, then the product gases contain only carbon dioxide, water vapour, and uncollected silica fume, and effluent treatment is greatly simplified.

There exists a wide range of potential siloxanes which may be used in the burners 33, but preferred siloxanes are the polymethylsiloxanes, including the linear polymethylsiloxane hexamethyldisiloxane, and the cyclic polymethylsiloxanes octamethylcyclotetrasiloxane, (OMCTS), and decamethylcyclopentasiloxane (DMCPS). Of the variety of alkoxysilanes which may alternatively be used, one of the preferred precursors is methyltrimethoxysilane (MTMS).

The product gases are led from the furnace via exhaust ducts 36, 37, their flow being controlled by means of valves 38, 39.

As noted, the refractory enclosure 35 serves as a crucible to contain the glass melt, and in the base of this crucible is an orifice 40 which may be defined by a die brick, or other die assembly 40a, constructed to form an exit which serves as a continuous casting nozzle through which molten glass is progressively drawn in the course of the process.

This die brick or die assembly may be made of a refractory material similar to that used to line the vessel 35, or may be made from another refractory material selected for improved erosion resistance, or may even be made from a refractory metal, optionally protected by a ceramic coating (e.g., molybdenum, coated with molybdenum disilicide). If a refractory metal die orifice is used, it is preferable to surround any exposed metal (e.g., the underside of the lip of the die) with a reducing gas, such as a hydrogen-nitrogen gas mixture.

Crucible 35 is supported, via appropriate insulating bricks 41, on a fixed base plate 42.

Beneath the orifice 40 depends a glass ingot 43, supported by a series of moveable clamps 44, which are designed during normal operation to move progressively downwards encouraging withdrawal of melt from crucible 35 at a selected rate, (e.g. corresponding to the rate at which synthetic silica glass is deposited from above by the array of burners 34). At intervals, each one of these clamps may be caused to release its grip from the ingot, and independently be driven upwards to the upper limit of its motion, before being adjusted once again to grip the descending ingot. In this way the clamps cycle up and slowly down, and the glass ingot is maintained under steady motion downwards. By ensuring that at all times the ingot is gripped by at least two clamps, the ingot is maintained entirely straight.

At intervals, a length of the glass ingot 43 may be cut off from its lower end, e.g., at point 45 accessible from mid-floor level 46, and then lowered to ground floor level 47, where it is released and removed for further processing.

By selecting the dimensions of the orifice 40 it is possible in this way continuously to form synthetic vitreous silica ingot of predetermined cross-section and dimensions,

thus it is possible to make cylindrical ingot, or ingot of square or rectangular cross-section, and even to extrude rectangle of high aspect ratio, i.e., plate. While for simplicity the base of crucible 35 is shown as substantially flat in Figure 3, for some applications it may be preferable to have an alternative shape, e.g., frusto-conical, to facilitate the flow of the glass to the orifice 40, to ensure an appropriate temperature distribution at the walls of the vessel, and to minimise devitrification at the walls, or around the orifice, which might otherwise affect the dimensions of the extruded ingot.

The process depicted in Figure 3 can be commenced as follows. The crucible 35 is assembled on the base plate 41, and a die assembly 40a is inserted. A previously manufactured ingot is raised via the clamps 44 into the orifice 40. This ingot may be machined if necessary to be an exact fit in the die orifice, and serves as a "bait-piece". The base of the crucible is covered with previously manufactured synthetic vitreous silica (e.g. in the form of lumps of glass). The furnace is brought to temperature by heating with the burner array, causing the initial furnace fill to melt and fuse to the upper end of the protruding bait-piece. Precursor material is then fed to the burners and, as deposition of glass proceeds, the melt level in the crucible 35 rises. When the desired melt depth is achieved, ingot retraction is commenced by starting the progressive downward motion of the clamps 42. Manufacture of ingot then continues as a steady process, with ingot withdrawal at least substantially matching glass deposition rate, and with ingot sections being cut off and removed at intervals as required (e.g. regular intervals).

The process depicted in Figure 3 is convenient for many applications requiring a glass ingot of high purity and controlled dimensions. However, as depicted, the crucible 35 is stationary, and it is evident that each burner 33 is directed at a fixed area of the surface of the melt. Glass deposited in this region thus has a slightly different

hydroxyl level than that deposited elsewhere, in cooler regions. If a chlorine-containing precursor material is used, then the chlorine content of the glass will be higher in the region of impact of each synthesis flame. These effects can result in minor inhomogeneities in the chemical properties and also in the refractive index of the glass ingot. For this reason it may be desirable to rotate the crucible 35 and ingot 43 in the course of the process and this is achieved via a development of the process, shown in Figure 4.

In this case the apparatus comprises a furnace enclosure 51, lined with refractory brick, and supporting a roof 52, also made of suitable refractory material. One or more burners 53 project through this roof. These burners may be made of metal or quartz glass, and are fed with fuel gases, oxygen, and precursor vapour as described above.

The product gases are led from the furnace via exhaust ducts 56, 57, their flow being controlled by means of valves 58, 59.

Again the product glass is collected in a refractory vessel or crucible assembly 55 in the base of which a shaping orifice 60, defined by a refractory die 60a made of one or more bricks, or alternatively a refractory metal plate as described above. The crucible assembly 55 is again supported on insulating bricks 61 and on a base plate 62, but in this case base plate 62 comprises a turntable, which is maintained at constant height, but is capable of rotation about a vertical axis.

Beneath the shaping orifice 60, depends a glass ingot 63, supported by a series of rotating chucks 64, which are designed to rotate synchronously with the crucible assembly 55, and turntable 62, but are also capable of progressive advance in a downward direction, all chucks moving at identical speed, thus permitting withdrawal of melt from the crucible assembly 55 at a chosen rate (preferably a constant

rate, corresponding to the rate at which synthetic silica glass is deposited by the array of burners above).

Again, as previously, each one of these chucks 64 may be caused to release its grip from the ingot 63, and can then be independently driven upwards to the upper limit of its motion, before being adjusted once again to grip the descending ingot. In this way the chucks 64 cycle up and slowly down, while rotating at constant speed, and the glass ingot is maintained with constant rotation and steady motion downwards. By using twin-jawed chucks 64 it is possible to ensure that the ingot 65 is maintained entirely straight.

At intervals, a length of glass ingot may be cut off, e.g., at point 65, at mid-floor level 66, and then lowered to ground floor level 67, where it is released and removed for further processing.

Again, by selecting the dimensions of the shaping orifice 60, it is possible continuously to form a synthetic vitreous silica ingot of predetermined cross-section and dimensions, thus it is possible to make a circular cylindrical ingot, or an ingot of square or rectangular cross- section, and even to extrude an ingot whose cross-section is a rectangle of high aspect ratio, i.e., plate. While for simplicity the base of the crucible assembly 55 is shown as substantially flat in Figure 4, for some applications it may be preferable to have an alternative shape, e.g., frusto-conical, to facilitate the flow the glass to the shaping orifice 60, to ensure an appropriate temperature distribution at the walls of the vessel, and to minimise devitrification at the walls, or around the orifice 60, which might otherwise affect the dimensions of the extruded ingot.

Because of the rotation of the crucible assembly 55, the burners 53 are depositing on a continuously moving surface, and this avoids overheating of any localised area on the glass surface, enhances the deposition efficiency and enables

a substantial increase in homogeneity of the glass deposited in the crucible assembly to be achieved. Additionally, the progressive motion of the glass through the crucible assembly to the orifice 60, permits mixing and diffusion processes which further enhance the homogeneity of the glass product.

An installation comprising the turntable 62, and the moving chucks 64, can be considered to be a large vertically-oriented lathe, of which the bed comprises a tower assembly 68. For the ultimate in homogeneity, it is possible to cause the supporting tower 68 to move horizontally to and fro in an x- direction, or even in both x- and y- directions these directions being mutually at right angles and at right angles to the direction Z of ingot withdrawal, but this is unnecessary for most applications of the glass ingot product. Alternatively, it is possible in principle to cause the furnace roof/burner assembly to oscillate slowly in the x-direction, and potentially in the x- and y- directions, to effect the same homogenisation process.

The choice of refractories is clearly important for successful operation of this type of process. In general high quality zircon refractories have proved adequate, but high purity is necessary to minimise contamination, especially when using chlorine-free precursors. Greater erosion resistance is however achieved when using yttria stabilised zirconia refractories, the added expense of which is justified by the increased longevity of the furnace components, and the efficiency of the process in enabling the manufacture on a continuous basis of an ingot of the required cross-section and dimensions.

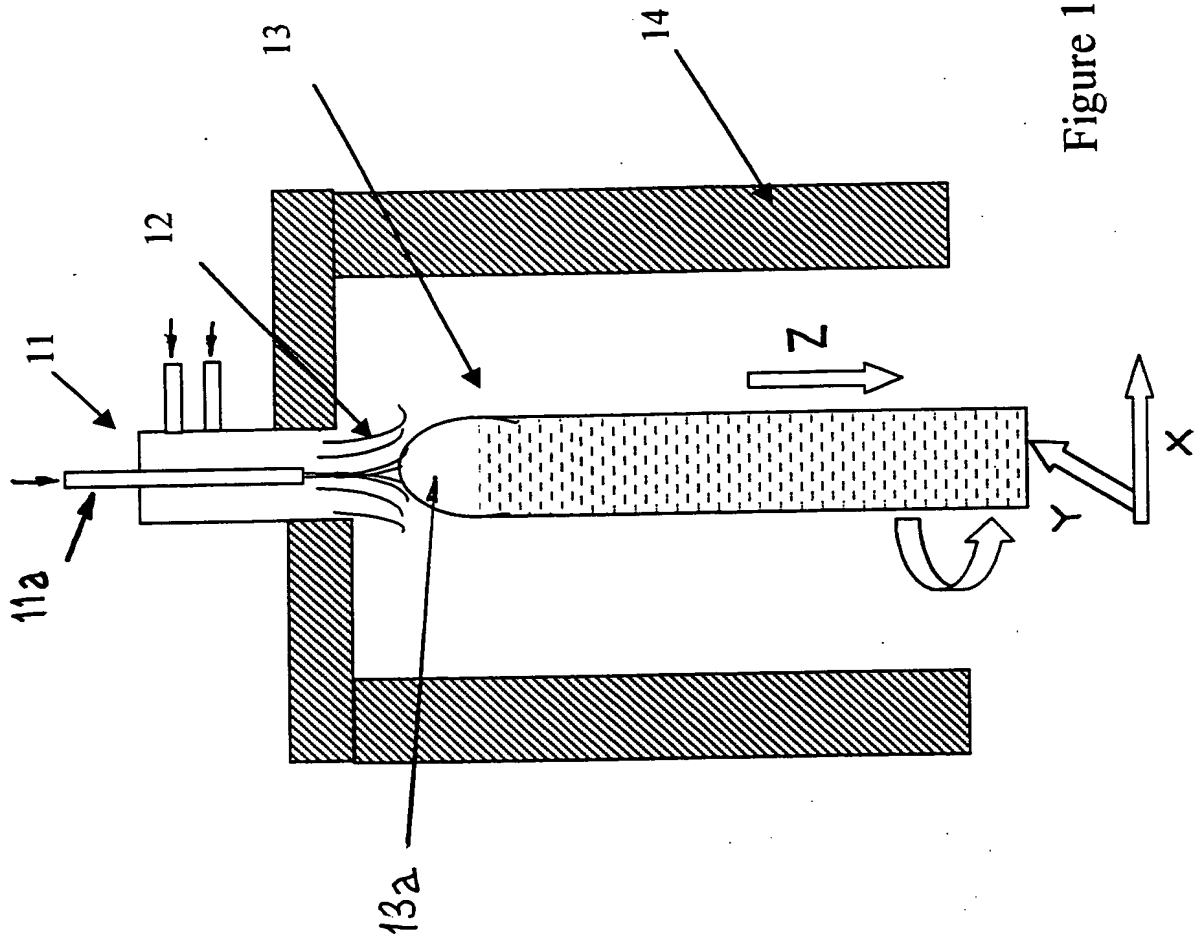

Figure 1

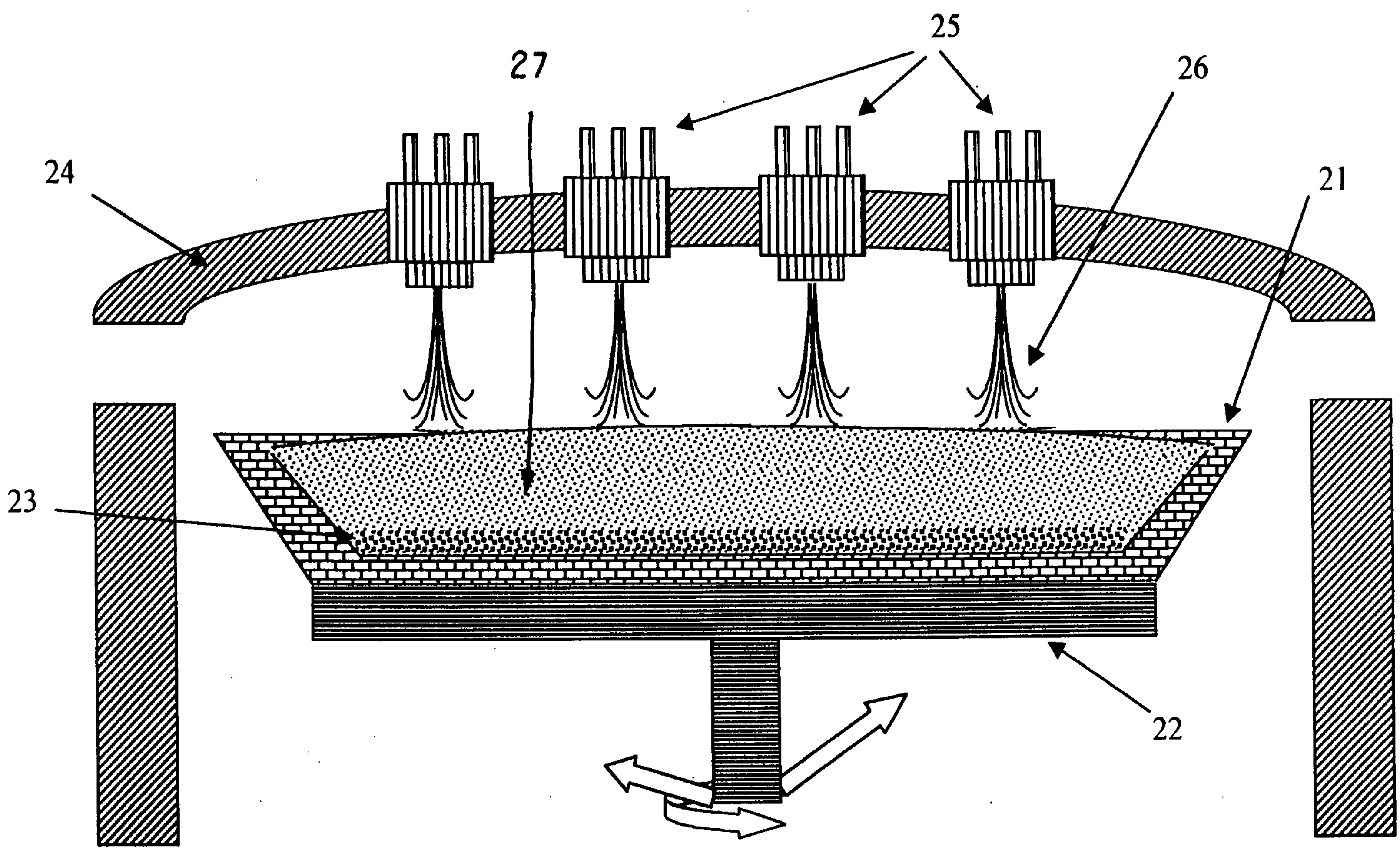

Figure 2

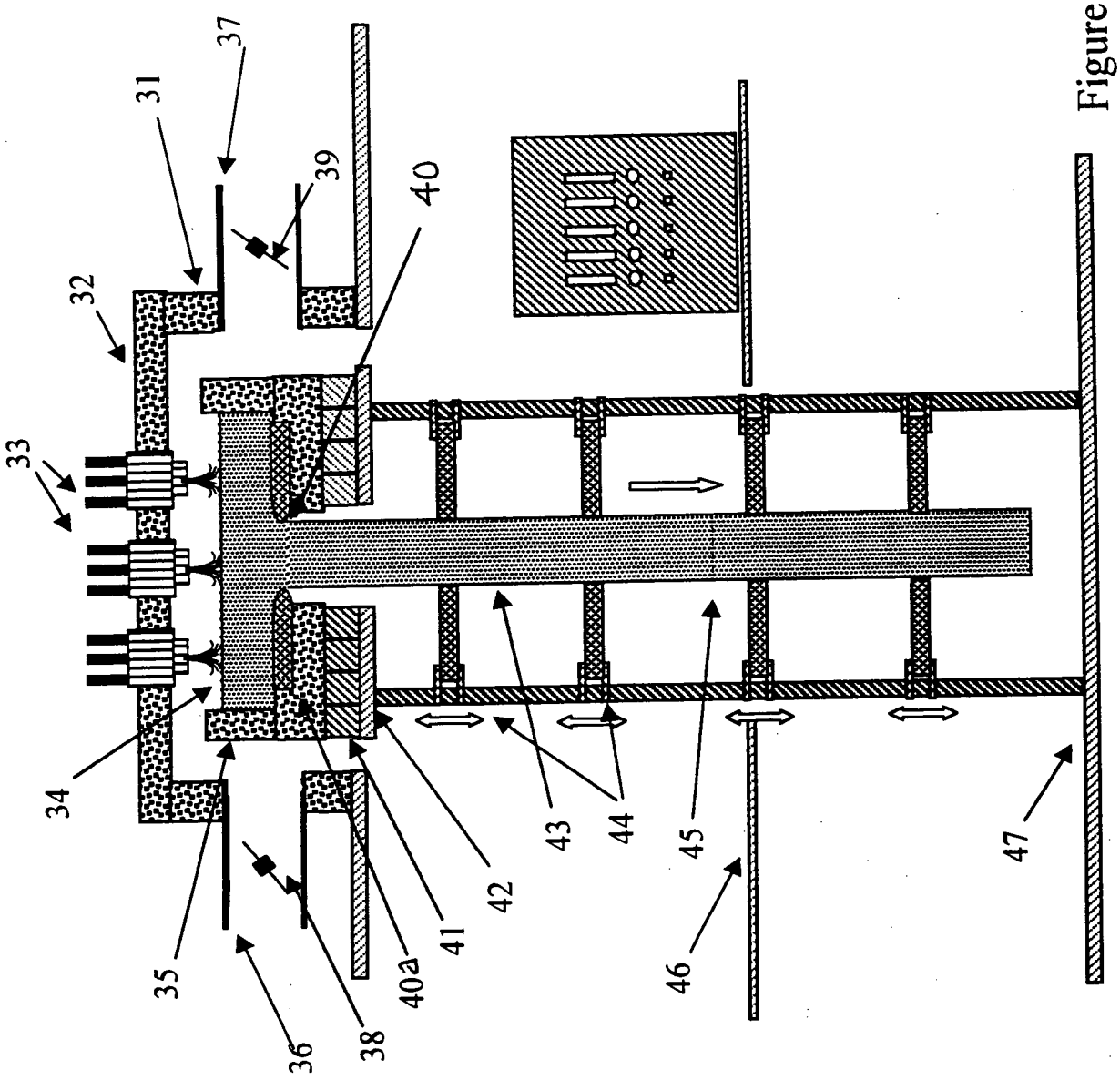

Figure 3

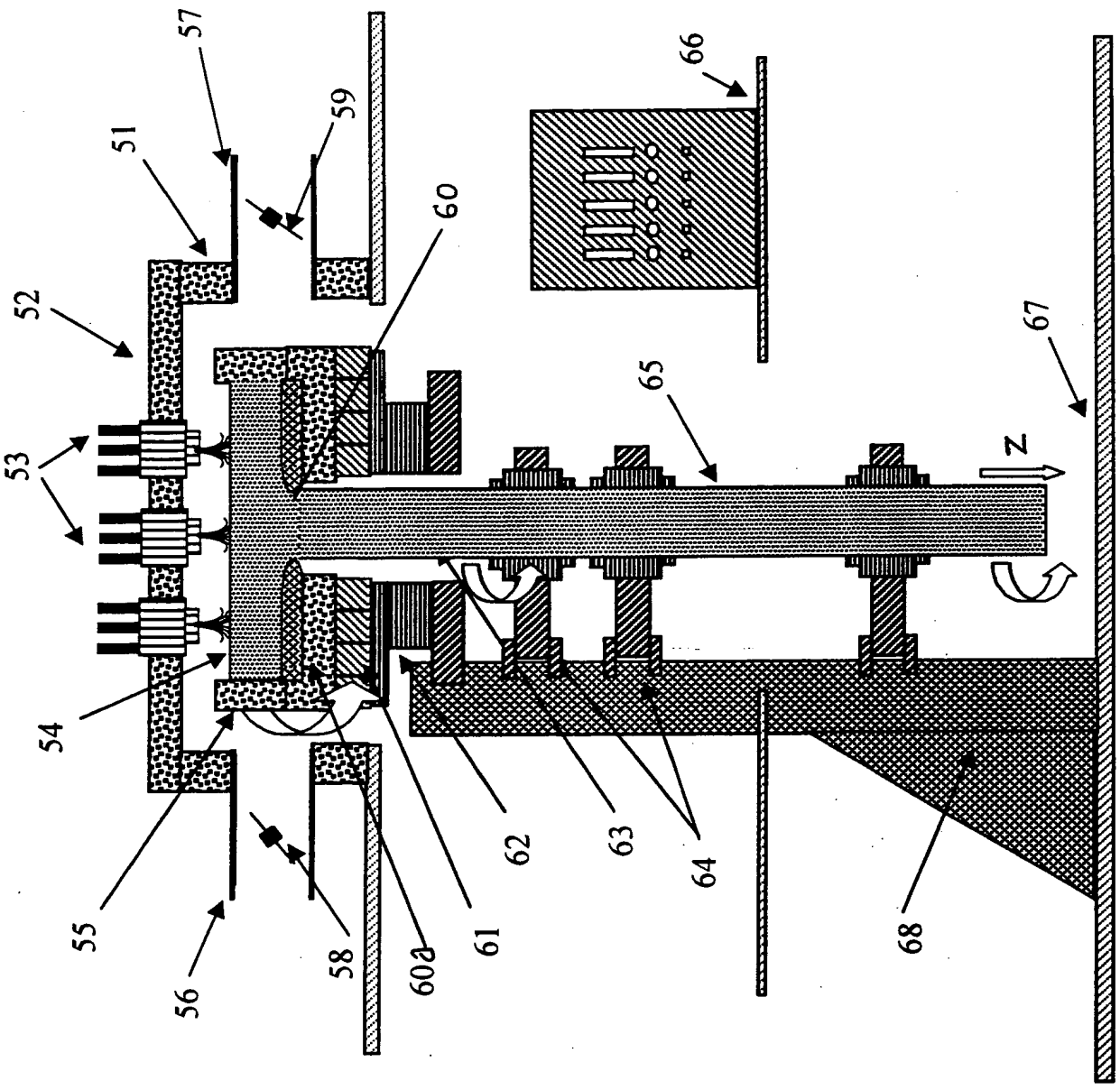

Figure 4

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